METHOD OF QUANTITATIVE EMISSION SPECTRAL ANALYSIS BASED ON THE MAXIMAL INTENSITY OF SPECTRAL LINES IN THE PROCESS OF BURNING A SUBSTANCE

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An empirical formula is derived for describing the change in the spectral line intensity during combustion of a measured quantity of substance under the effect of an electric discharge, based on the correlation between intensity at the instant of intensity increase, rate of burning, rate of increase in intensity under the experimental conditions used, and time. The formula is applied to quantitative emission analysis of a measured substance and to analysis of monolithic specimens of copper-zinc alloys of differing zinc contents. The method, based on the maximum line intensity during combustion of the substance, permits an increase in sensitivity and a reduction in time of spectral analysis over conventional methods using the integral line intensity without time resolution of the spectra.

The method of total combustion of a measured quantity of a substance applied to electrodes is often used in spectral analysis.

On the basis of the method of "spectral energies" the integral intensity of the spectral lines of the studied element, obtained upon complete combustion of the analyzed substance, is taken as a measure of the concentration of the element in the sample.

Our investigations (Ref.1) showed that a change in the intensity of the spectral line during burning of a measured quantity of substance under the effect of an electric discharge can be described empirically by the derived dependence

$$i = i_0 e^{-\alpha t}(1 - e^{-\beta t}), \tag{1}$$

where i is the intensity of the spectral line; i_0 is the intensity of the spectral line at the initial instant for the case of an instantaneous increase in intensity; α and β are constants respectively characterizing the rate of burning of the substance and the rate of increase in intensity of the spectral line and dependent on the conditions of analysis; t is the time.

According to eq.(1), the integral intensity of the spectral line upon com-

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** Numbers given in the margin indicate pagination in the original foreign text.

plete burn-up of the substance is equal to

$$I = \int_0^\infty i\,dt = i_0 \frac{\beta}{\alpha(\alpha+\beta)}.$$ (2)

It also follows from eq.(1) that during burning of the substance the intensity of the spectral line reaches a maximum value equal to

$$i_{max} = i_0 \frac{\beta}{\alpha+\beta}\left(\frac{\alpha}{\alpha+\beta}\right)^{\alpha/\beta}.$$ (3)

and then decreases.

A comparison of eqs.(2) and (3) shows that the maximum intensity is proportional to the integral intensity

$$i_{max} = i_0 \frac{\beta}{\alpha(\alpha+\beta)}\,\alpha\left(\frac{\alpha}{\alpha+\beta}\right)^{\alpha/\beta} = I\,\alpha\left(\frac{\alpha}{\alpha+\beta}\right)^{\alpha/\beta}.$$ (4)

Thus, not only the integral but also the maximum intensity of the spec- /373 tral line can serve as a criterion for the concentration of the element being determined in a quantitative emission spectral analysis. To record the maximum intensity of the spectral line, the method of spectrometry with time resolution is used.

In view of the existence of an analogy between processes of burning of a measured quantity of substance and processes of roasting (Ref.2), the initial stage of the latter, including the instant of onset of maximum intensity, can also be described by eq.(1). This justifies use of the proposed method not only for analyzing a measured quantity of substance but also for analyzing monolithic specimens.

The presence of a concentration sensitivity to the maximum intensity of the spectral line is illustrated in Fig.1, where the time rate of change of the line intensity of Zn I 4810 Å is given for the case of combustion of a measured quantity of substance and for the case of roasting of monolithic specimens of copper-zinc alloys with different zinc contents.

Figure 2 shows calibration curves for a quantitative determination of Cr, Ba, Zn, Mn, Ag, and Pb in solutions and of Mn, Cr, Zn, and Ni in alloys of monolithic specimens, plotted from our proposed methods in coordinates $\log i_{max}$ - - $\log C$. The experimental data were obtained on a photoelectric stylometer FES-1. As spectrum excitation source we used a generator with a GEU-1 electronic control. The change in intensity of the spectral line during burning of the substance was recorded on an EPP-09 electronic potentiometer. An FEU-18A photomultiplier was used as radiation receiver. To fatigue the photocathode and check the sensitivity of the circuit we used a miniature 3.5-volt bulb LN whose

light, prior to the measurements and in the intervals between measurements, was made to strike the photomultiplier. The bulb was powered from a battery. A special circuit made it possible to regulate the filament current and to break the supply circuit of the bulb at the required instant of time.
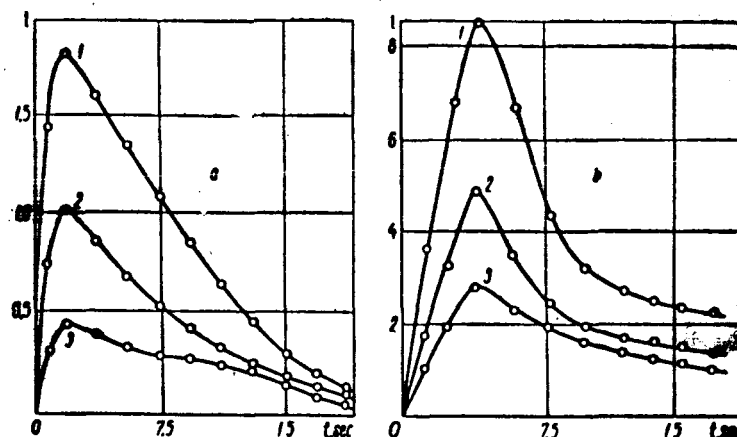

Fig.1 Change in the Intensity of the Spectral Line of
Zn I 4810 Å during Burning of a Measured Quantity
of Substance.
a - 1) 2×10^{-5} gm, 2) 10^{-5} gm, 3) 5×10^{-6} gm, and
during roasting of monolithic specimens; b - 1) 2%,
2) 17%, 3) 7%.

Solutions of Mn, Pb, Zn were analyzed under alternating-current arc conditions at a current of 2 - 3 amp and 90° ignition phase, while Ag, Ba, and Cr were analyzed in a low-voltage spark with a capacitance of 20 - 40 μf and zero inductance.

The investigated chemical elements, from a solution of the sample, were /374 applied in drops to depressions made in copper electrodes. On drying, this ensured a concentration of the dry residue over a small area. To firmly attach the latter, an aqueous solution of sucrose was used.

The monolithic specimens were investigated under polar conditions of the arc and a low-voltage spark. Zinc was analyzed in an arc at a current strength of 1 amp, while manganese, chromium, and nickel were tested in a spark with a capacitance of 20 - 40 μf and zero inductance. In all cases, the sample served as the cathode. · The given conditions are characterized by a localized striking of the specimen, which permits obtaining well-defined intensity maxima at the initial instant of discharge.

Tapered copper rods served as the supporting electrodes for analyzing the solutions and monolithic specimens. The analytical interval was set at 1.5 mm.

This method permitted us to obtain a sufficiently good reproducibility of the experimental results.
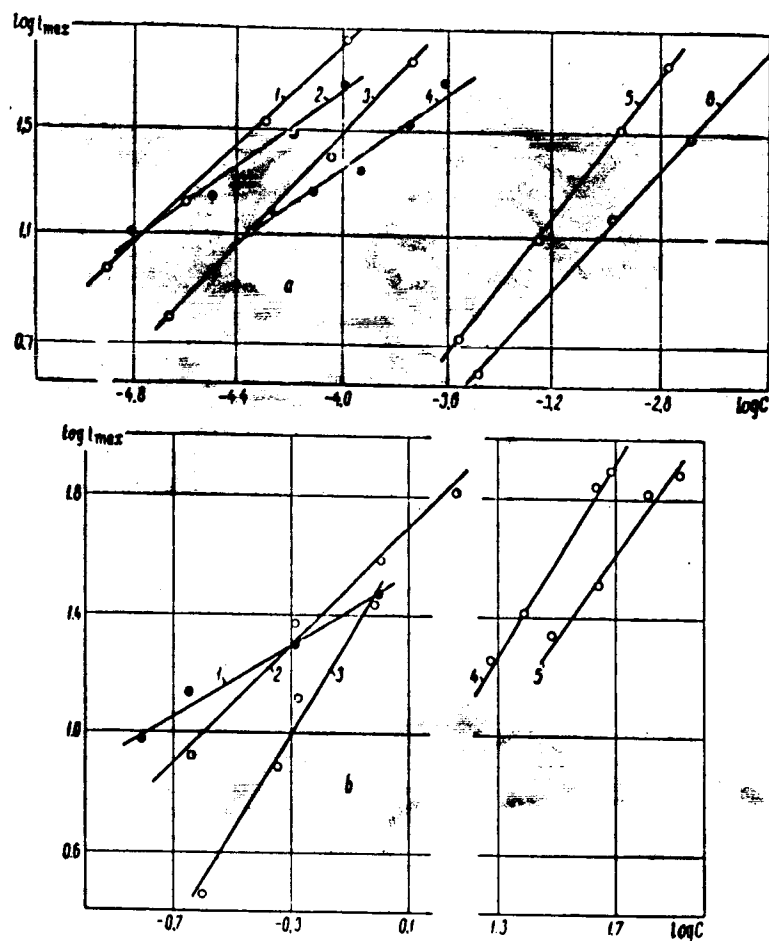
Fig.2 Calibration Curves.
a – For analysis of solutions: 1) Cr I 4254.33 Å;
2) Ba II 4554.04 Å; 3) Zn I 4810.54 Å;
4) Mn I 4783.4 Å; 5) Ag I 5209.07 Å;
6) Pb I 4057.82 Å;
b – For analysis of monolithic specimens:
1) Mn I 4783.4 Å (Alumel alloy, set of standards
No.7); 2) Cr I 5204.5 Å; 3) Mn I 4783.4 Å
(steel, set of standards No.5); 4) Zn I 4810.4 Å
(Cu–Zn alloy); 5) Ni I 4714.4 Å (Cu–Ni alloy).

The method of quantitative emission spectral analysis, based on the $\underline{/375}$
maximum intensity of the spectral line during the burning of a substance, per-
mits increasing the sensitivity and reducing the time of analysis in comparison
with ordinary methods of spectral analysis which utilize the integral intensity
of spectral lines without time resolution of the spectra.

The higher sensitivity of spectral analyses by the proposed method is due
to the fact that, during burning of a substance, the maximum ratio of line in-
tensity to background intensity is reached at the instant of maximum intensity
of the spectral line. This ratio is smaller in conventional methods of analysis

that do not use time resolution when recording the intensity of the spectra.

Thus, less time for analysis is needed with our methods since complete combustion of the investigated specimen is not necessary when analyzing a measured quantity of the substance. When analyzing monolithic specimens there is no need to conduct preliminary roasting since the concentration is determined at the initial stage of roasting. Thus, in both cases the exposure time is reduced.

It should be pointed out that any change in the spectral line intensity during combustion of the substance, including the maximum line intensity for monolithic specimens, depends on the processes of entry of the substance. Good calibration curves are obtained when the so-called "regular" entry of the substance is observed, i.e., when direct proportionality exists between concentration of the investigated element in the specimen and in the discharge cloud.

In the presence of mutual influence of the elements, the "regular" entry of the substance is disrupted and the calibration curves are not always rectilinear. Such dependences are observed in spectral analyses based on the maximum line intensity for silicon brasses and copper-nickel binary alloys. Thus, in the method of spectral analysis based on the maximum intensity of spectral lines it is necessary to develop ways and means of eliminating or taking into account mutual effects of elements.

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